Metal ion dissolution from high-capacity LiNi_{0.8}Co_{0.16}Al_{0.04}O_{2} cathode materials during storage at 90°C was completely blocked by a lithium-reactive Co_{3}(PO_{4})_{2} nanoparticle coating. As opposed to conventional coating methods, in which the coating material did not react with LiOH and Li_{2}CO_{3} impurities dissolved from the cathode, the Co_{3}(PO_{4})_{2} coating material reacted with such impurities during annealing to form an olivine LiCoPO_{4} phase on the bulk surface. Electrochemical properties of the optimized sample, annealed at 700°C for 5 h, demonstrated a 30% enhancement of the cycle life, compared to a bare sample without a loss in the first discharge capacity. Storage tests of the 4.3 V charged electrode at 90°C after 7 days showed that the bare sample was transformed into the spinel phase with a Fd3m space group, whereas the Co_{3}(PO_{4})_{2}-coated sample remained as a layered hexagonal phase with an R3m space group.

**Experimental**

In order to precipitate Co_{3}(PO_{4})_{2} nanoparticles, 0.38 g cobalt nitrate and 1 g (NH_{4})_{2}HPO_{4} were dissolved in 30 mL distilled water. The nanoparticles, which were instantly pink in color and precipitated in the solution, were stirred for 20 min at pH ~ 5. To this solution, 100 g LiNi_{0.8}Co_{0.16}Al_{0.04}O_{2} powder was added and mixed for 10 min, followed by drying and annealing at 120 and 700°C for 12 and 5 h, respectively, in air. LiNi_{0.8}Co_{0.16}Al_{0.04}O_{2} powder with a particle size of 13 µm was prepared by mixing stoichiometric amounts of coprecipitated Ni_{0.86}Co_{0.16}Al_{0.04}OH(OH) and LiOH·H_{2}O that were fired at 480 and 780°C for 4 and 15 h, respectively, at a molar ratio of 1:1.02. The detailed coprecipitation method of Ni_{0.86}Co_{0.16}Al_{0.04}OH(OH) is described in Ref. 9. Figure 1 shows a schematic flow diagram for conventional AlPO_{4} and Co_{3}(PO_{4})_{2} coating procedures for LiNi_{0.86}Co_{0.16}Al_{0.04}O_{2}. In the case of the AlPO_{4} coating, in order to minimize the gelation and swelling from the decomposition of Li impurities on the particle surface at elevated temperatures, a washing procedure is required, whereas Co_{3}(PO_{4})_{2} does not need a washing process due to the reaction between the coating material and Li sources. Overall, the latter method is much more economical than the first one. The change in the pH of the powders (bare, AlPO_{4}, and Co_{3}(PO_{4})_{2}-coated samples after annealing at 700°C) immersed in water was monitored by adding 20 g powder to 50 mL purified water (pH ~ 7) with constant stirring with a magnetic stirrer. The pH was measured over a 40 min period. The powder was recovered by filtration when the pH had stabilized. In
order to determine the moisture content (OH⁻) in the sample, a Karl-Fisher moisture titrator was used at 250°C (prior to measuring, the sample was vacuum-dried at 150°C for 2 h to remove the H₂O molecules adsorbed on the sample).

The cathodes for the battery test cells were made of cathode, super P carbon black, and polyvinylidene difluoride (PVDF) binder (Solef) in a weight ratio of 96:2:2. The slurry was prepared by thoroughly mixing an N-methyl-2-pyrrolidone (NMP) (Aldrich) solution of PVDF, carbon black, and the cathode material. The coin-type half cells (2016R size), prepared in a helium-filled glove box, contained a cathode, a Li metal anode, a microporous polyethylene separator, and an electrolyte solution of 1 M LiPF₆ in ethylene carbonate/dimethyl carbonate (EC/DMC) (1:1 vol %).

High-resolution transmission electron microscopy (HRTEM) samples were prepared by the evaporation of the dispersed nanoparticles in acetone or hexane on carbon-coated copper grids. The field-emission electron microscope was a JEOL 2000F operating at 200 kV. Powder X-ray diffraction (XRD) measurements were carried out using a Rigaku D/Max2000 with a Cu target tube. Inductively coupled plasma mass spectroscopy (ICP-MS; ICPS-1000IV, Shimadzu) was used to determine the metal content.

Results and Discussion

In order to confirm the possible formation of the LiCoPO₄ layer on the LiNi₀.₈Co₀.₁₆Al₀.₀₄O₂ powder, a mixture of 0.02 g LiOH·H₂O and 0.02 g LiCoPO₄ nanoparticles was precipitated and annealed at 700°C for 7 h. The precipitated material was identified as a pure olivine phase by XRD analysis. If any impurities were present, they were identified and quantified using ICP-MS analysis of the sample.

Figure 2 exhibits the XRD patterns of precipitated Co₃(PO₄)₂ nanoparticles and as-prepared LiCoPO₄, using firing of the mixture of 0.02 g LiOH·H₂O and 0.02 g Co₃(PO₄)₂ nanoparticles at 700°C for 7 h.

Li impurities, however, cannot be eliminated by the formation of additional Li contribution from the bulk during the formation of LiCoPO₄, as well as possible formation of the solid solution phase between LiCoPO₄ and the bulk. Figure 3 shows TEM images of the bare and Co₃(PO₄)₂-coated sample surfaces, and the bare sample did not show any coating layer, as usually observed in coated samples. 24-32 Coating concentration of the sample after annealing at 700°C was estimated to be ~1 wt % by using ICP-MS analysis of the P element. The d-spacing value of the bare sample corresponds to (104) lattice fringes of the layered hexagonal phase. The coated sample showed 3.45 and 2.49 Å d-spacing values at the particle surface, corresponding to (111) and (311) lattice fringes of the olivine LiCoPO₄ phase, respectively, 24 confirming the above assumption. Previously our result showed that the 1 wt % AlPO₄ coating concentration approximately corresponded to ~20 nm coating thickness. 31 However, the AlPO₄ coating layer did not react with the bulk phase during annealing, thus forming a distinguishable coating layer to the bulk phase. However, in the case of Co₃(PO₄)₂ coating, the coating layer reacted with Li impurities such as LiOH and Li₂CO₃ and Li in the bulk, resulting in the formation of Li₄CoPO₄. Accordingly, the Li₄CoPO₄ coating layer is not easy to distinguish from the bulk phase, as supported by Fig. 3.

Figure 4 shows XRD patterns of the bare and coated cathode powders and phase can be indexed with hexagonal-type layered structure with an R₃m space group without showing secondary
phases. Lattice constants \( a \) and \( c \) of the bare and coated sample are quite similar to each other, showing \( a = 2.8631(4) \), \( c = 14.165(7) \) and \( a = 2.8621(6), \ c = 14.164(3) \), respectively.

Figure 5 exhibits the voltage profiles of the bare and the coated samples annealed at 700°C for 5 h at 0.1, 0.2, 0.5, and 1 C rates and after 40 cycles at a rate of 1 C between 3 and 4.3 V (1 C rate was set at 190 mA/g). After coating, the first discharge capacity and irreversible capacity ratio of 190 mAh/g and 10%, respectively, were similar to the bare sample. (The discharge curves were obtained from using the same sample.) However, the discharge capacity of the first 1 C cycling was 173 mAh/g, which is higher than the bare sample (160 mAh/g), and the capacity retention of the coated samples after 40 cycles was 149 mAh/g, which is 30% higher than the bare sample. Olivine-type material is known to have low electron conductivity, but this is the case for the bulk material. In our case, the electrical conductivity of the nanometer-scale olivine coating layer is believed to be much improved, compared with the bulk analogue, because the C-rate performance of the coated sample was not affected by the coating layer, as shown in Fig. 5b. Such improvement is believed to be that the nanometer-scale olivine layer helps the electrical conduction due to the reduced surface scattering that enhanced the total resistivity of the material.35

Figure 6 shows the pH changes in the bare and Co\(_3\)(PO\(_4\))\(_2\)-coated samples, compared with a AlPO\(_4\)-coated sample. After coating, the first discharge capacity and first 1 C cycling was 173 mAh/g, which is higher than the bare sample. Olivine-type materials are dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the other hand, were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathodes were dissolved into the solution, and lithium impurities on the cathode material during storage. Correspondingly, lattice oxygen O\(^2-\) is oxidized to active oxygen O\(^3-\), followed by the weakening of the Ni-O bond. Then, a disproportionating reaction of active oxygen O\(^3-\) produced on the surface combines with CO\(_2\) and H\(_2\)O in air to form Li\(_2\)CO\(_3\) and LiOH on the surface of the cathode. This oxygen undergoes reactions with CO\(_2\)/H\(_2\)O in air, according to the following reaction

\[
\text{O}^{2-} + \text{CO}_2\text{H}_2\text{O} \rightarrow \text{CO}_3^{2-}/2\text{OH}^{-}
\]

which is believed to react with LiPF\(_6\), producing acidic HF in the electrolytes. HF can then easily dissolve the Ni\(^{3+}\) and Co\(^{3+}\) metal ions. This result indicates that the olivine LiCoPO\(_4\) phase is very effective in minimizing metal dissolution.

Figure 7 exhibits XRD patterns of the bare electrode before and after charging at 4.3 V under various conditions. When the layered phase is transformed to the spinel phase, two sets of (006)/(102) and (018)/(110) peaks merge into the single ones. In addition, a peak at ~18.5° (marked as ▼ in Fig. 7) shifts to higher angles. Because the (110) peak is superimposed with an Al peak at 65° (dotted lines in Fig. 6 and 7), the merging (018) and (110) peaks into the single peak is not readily observed in the bare and coated samples, especially the samples stored at 90°C. However, the change of the peak distance between the (018) and (110) peaks in the XRD pattern after charging the cell and kept in electrolytes during storage, using both the bare and the coated samples, were monitored for the following conditions: 1 and 7 days at room temperature and 90°C, as well as 1 and 7 days at 90°C after 4.3 V charging. After charging the cells, the electrodes were separated from the cell and kept in electrolytes (10 mL) for designated
times. Both bare and coated samples did not show any noticeable metal dissolution, even after storage at 90°C for 1 day (4.3 V charging). However, the amounts of Co and Ni ions dissolved increased to 90 and 250 ppm, respectively, after 7 days of storage at 90°C after 4.3 V charging. The coated samples stored at 90°C for 1 day after 4.3 V charging resulted in negligible amounts of Ni and Co ions dissolved, which were 1.2 and 2.4 ppm, respectively, after 7 days at 90°C. We believe that such Ni⁴⁺ ion dissolution initiates structural rearrangement from the layered to the spinel phase. We further carried out TEM analysis of the charged bare sample after storage at 90°C for 7 days, as shown in Fig. 8. Figure 8a shows the surface morphology of the stored sample and many surface roughnesses can be observed. This is indicative of surface defects generated by the Ni⁴⁺ ion dissolution. Figure 8b exhibits the HRTEM image of Fig. 8a, and a lattice fringe of the (311) plane corresponding to 2.42 Å of spinel LiNi₂O₄ phase.

After storage at 90°C for 7 days, all the diffraction peaks are assigned to a spinel phase with a lattice constant of 8.083 Å. In general, the transformation of the layered structure with an R₃̅ₐ space group to the spinel phase (Fd₃m) requires a migration of 25% of the transition metal ions from 3b octahedral sites (metal layer) into 3a octahedral sites (lithium layer). Our Rietveld refinement result showed 10% of the (Ni,Co)³⁺/⁴⁺ ions in the 16C sites, indicating that the migration of the transition metal ions from the nickel layer into the lithium layer to produce a spinel structure is incomplete at 90°C. This is the first evidence for the phase transformation to a spinel phase at the very low temperature of 90°C, as compared with previous studies that showed the spinel transition above 150°C.⁴ The calculation of the cation migration of the bare sample after storage is based on spinel structure because its XRD pattern supported the phase transformation into the spinel.

The XRD patterns of the coated samples stored at 90°C for 1 and 7 days are different from those of the bare samples at the same storage condition and do not show the peaks merging in two sets of (018)/(110) and (006)/(102) peaks (Fig. 9). Generally, (006) and (102) peaks get to merge with delithiation in the cathode material, but the coated sample still shows the peaks splitting. At this time, we do not know the origin of such phenomena, but we suspect that coating may affect the microstructure of the cathode material. In addition, peaks shifted to higher angles are not observed. These results mean that the coated sample did not show the phase transition to a spinel phase even after 7 days of storage at 90°C after 4.3 V charging. Because the XRD pattern of the coated cathodes after 7 days storage at 4.3 V could be indexed with a hexagonal-type layered structure with an R₃m space, we did not consider the possible cation migration that led to structural transformation into the spinel phase. The structural transformation starts on the particle surface by the metal dissolution and chemically stable LiCoPO₄ phase is effective to reduce the metal dissolution. The TEM images of the stored cathode in Fig. 10 show smooth surfaces, as opposed to those of the bare cathode (Fig. 8), and a lattice fringe of the (311) plane of the LiCoPO₄ phase corresponding to 2.50 Å is observed.

Table 1. ICP-MS results of Ni and Co in the charged bare and coated charged samples stored at 90°C for 1 and 7 days.

<table>
<thead>
<tr>
<th></th>
<th>Ni (ppm)</th>
<th>Co (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare sample</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Before storage</td>
<td>2</td>
<td>1.8</td>
</tr>
<tr>
<td>After 1 day</td>
<td>9.7</td>
<td>3.4</td>
</tr>
<tr>
<td>After 7 days</td>
<td>250</td>
<td>90</td>
</tr>
<tr>
<td>Coated sample</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Before storage</td>
<td>0.9</td>
<td>1.4</td>
</tr>
<tr>
<td>After 1 day</td>
<td>1.2</td>
<td>2.2</td>
</tr>
<tr>
<td>After 7 days</td>
<td>1.4</td>
<td>2.4</td>
</tr>
</tbody>
</table>
the Co\textsubscript{3}ing methods that could not remove the LiOH and Li\textsubscript{2}CO\textsubscript{3} impurities, the bare cathode was transformed into the spinel phase, possibly due to prolonged storage at 90°C for 7 days. Upon prolonged storage of the charged cathode

Figure 9. XRD patterns of the coated electrode before charging and after charging at 4.3 V at various conditions.

**Conclusion**

A lithium-reactive Co\textsubscript{3}(PO\textsubscript{4})\textsubscript{2} nanoparticle coating LiNi\textsubscript{0.8}Co\textsubscript{0.16}A\textsubscript{0.04}O\textsubscript{2} resulted in the formation of a Li\textsubscript{x}CoPO\textsubscript{4} coating layer after annealing at 700°C. As opposed to conventional coating methods that could not remove the LiOH and Li\textsubscript{2}CO\textsubscript{3} impurities, the Co\textsubscript{3}(PO\textsubscript{4})\textsubscript{2} coating reacted with such impurities during the annealing process, thus minimizing any side reactions with electrolytes. Upon prolonged storage of the charged cathode (4.3 V) at 90°C, the coated cathode sustained the original layered phase while the bare cathode was transformed into the spinel phase, possibly due to the dissolution of Ni\textsuperscript{2+} ions into the electrolytes.

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**References**


Figure 10. TEM images of the coated electrode after charging at 4.3 V and subsequent storage at 90°C for 7 days.